

Set of equations for transient enhanced diffusion in shallow ion-implanted layers

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Abstract. To simulate the transient enhanced diffusion near the surface or interface, a set of equations describing the impurity diffusion and quasichemical reactions of dopant atoms and point defects in shallow ion-implanted layers is proposed and analyzed. The diffusion equations obtained take into account different charge states of mobile or immobile species and drift the mobile species in the built-in electric field and field of elastic stresses. The absorption of self-interstitials on the surface and drift of the defects due to elastic stresses result in the nonuniform distributions of point defects. It was shown analytically and by means of numerical calculations that consideration of the nonuniform defect distributions enables one to explain the phenomenon of “uphill” impurity diffusion near the surface during annealing of ion-implanted layers. The performed calculations of the boron concentration profile after annealing of a shallow implanted layer agree well with the experimental data confirming the efficiency of the proposed equations.

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1 Introduction

Using low-energy high-fluence ion implantation with the following rapid thermal annealing, one can produce the active regions of silicon devices characterized by very shallow junctions ($\sim 0.1 \mu\text{m}$) and high dopant concentrations [1, 2, 3]. During annealing the transient enhanced diffusion (TED) occurs. Therefore, the final dopant distribution is determined both by ion implantation and transient enhanced diffusion parameters. As the lateral dimensions of integrated circuits are scaled down to the submicrometer range, the need for accurate modeling of silicon doping is increased. The well-known and widely used models of TED during rapid thermal annealing of semiconductor substrates very often lead to the results which disagree with the experimental data for low-energy high-dose ion implantation, especially in the near surface region. For example, the calculations presented in Refs. [1, 2] provide some evidence of disagreement with the experimental data in the vicinity of the interface. The difference is mainly due to the use of inadequate clustering models for the description of high concentration diffusion [4], due to the influence of interfaces on the defect distributions [5], due to dopant atom trapping by immobile sinks [6], and due to the influence of stresses on the dopant and defect diffusion [7, 8]. The principal goal of this investigation is to obtain a set of equations describing

impurity diffusion and quasichemical reactions of dopant atoms and point defects near the surface or interface to simulate adequately the transient enhanced diffusion in shallow implanted layers.

2 System of equations

It is proposed that during the initial stage of annealing the ion-implanted silicon substrates a thin damaged layer is formed near the surface or in the vicinity of the interface. For example, such a damaged layer can be formed due to incomplete solid phase recrystallization of silicon regions heavily doped by As [9] or due to the near surface absorption of mobile point defects created by boron implantation. During annealing this damaged layer can absorb mobile point defects and impurity atoms, that results in the formation of nonuniform defect distributions and electrical deactivation of impurity. Moreover, if the damaged layer contains a great amount of defects and impurity atoms, significant stresses can arise in the region adjoined to the surface. To describe diffusion of point defects and impurity atoms in this intricate system, the following set of equations is proposed:

1. Expression for the total concentration of impurity atoms C^T

$$C^T = C + C^{AC} + C^{AD} \quad , \quad (1)$$

where C is the concentration of substitutionally dissolved impurity atoms, C^{AC} and C^{AD} are the concentrations of impurity atoms incorporated into clusters and bound to the extended defects, respectively;

2. Conservation law for impurity atoms incorporated into clusters (precipitates)

$$\frac{\partial C^{AC}}{\partial t} = S^{AC} - G^{AC} \quad . \quad (2)$$

3. Conservation law for impurity atoms bound to the extended defects

$$\frac{\partial C^{AD}}{\partial t} = S^{AD} - G^{AD} \quad . \quad (3)$$

4. Equation of diffusion for impurity atoms due to the formation, migration, and dissociation of the pairs “impurity atom — point defect” which are in equilibrium with the substitutionally dissolved impurity atoms and point defects [10]. For the two-stream diffusion govern by the vacancies and self-interstitials this equation has the form

$$\begin{aligned} \frac{\partial C}{\partial t} = & \left[D^E \frac{\partial (a^E \tilde{C}^{V \times} C)}{\partial x} + \frac{D^E a^E \tilde{C}^{V \times} C}{\chi} \frac{\partial \chi}{\partial x} \right] - \frac{\partial}{\partial x} (v_x^E a^E \tilde{C}^{V \times} C) \\ & + \frac{\partial}{\partial x} \left[D^F \frac{\partial (a^F \tilde{C}^{I \times} C)}{\partial x} + \frac{D^F a^F \tilde{C}^{I \times} C}{\chi} \frac{\partial \chi}{\partial x} \right] \\ & - \frac{\partial}{\partial x} (v_x^F a^F \tilde{C}^{I \times} C) - S^A + G^A \end{aligned} \quad . \quad (4)$$

5. Equation of vacancy diffusion [11]

$$\begin{aligned} \frac{\partial}{\partial x} \left[d^{VC}(\chi) \frac{\partial (a^{Vd} \tilde{C}^{V\times})}{\partial x} \right] - \frac{\partial}{\partial x} \left(\tilde{v}_x^V \tilde{C}^{V\times} \right) - \\ - \frac{k^{VC}}{(l_i^V)^2} \tilde{C}^{V\times} + \frac{\tilde{g}^V}{(l_i^V)^2} = 0 \end{aligned} \quad (5)$$

6. Equation for diffusion of self-interstitials [11]

$$\begin{aligned} \frac{\partial}{\partial x} \left[d^{IC}(\chi) \frac{\partial (a^{Id} \tilde{C}^{I\times})}{\partial x} \right] - \frac{\partial}{\partial x} \left(\tilde{v}_x^I \tilde{C}^{I\times} \right) - \\ - \frac{k^{IC}}{(l_i^I)^2} \tilde{C}^{I\times} + \frac{\tilde{g}^I}{(l_i^I)^2} = 0 \end{aligned} \quad (6)$$

where the effective coefficients of the equations are presented as follows:

$$D^E(\chi) = D_i^E \frac{1 + \beta_1^E \chi + \beta_2^E \chi^2}{1 + \beta_1^E + \beta_2^E} \quad , \quad (7)$$

$$D^F(\chi) = D_i^F \frac{1 + \beta_1^F \chi + \beta_2^F \chi^2}{1 + \beta_1^F + \beta_2^F} \quad , \quad (8)$$

$$\chi = \frac{C + \frac{z^{Cl}}{m} C^{AC} - C^B + \sqrt{\left(C + \frac{z^{Cl}}{m} C^{AC} - C^B \right)^2 + 4n_i^2}}{2n_i} \quad , \quad (9)$$

$$\tilde{C}^{V\times} = \frac{C^{V\times}}{C_{eq}^{V\times}} \quad , \quad \tilde{C}^{I\times} = \frac{C^{I\times}}{C_{eq}^{I\times}} \quad , \quad (10)$$

$$d^{VC,IC}(\chi) = \frac{d^{V,I}(\chi)}{d_i^{V,I}} \quad , \quad k^{VC,IC} = k^{V,I} \tau_i^{V,I} \quad , \quad (11)$$

$$l_i^V = \sqrt{d_i^V \tau_i^V} \quad , \quad l_i^I = \sqrt{d_i^I \tau_i^I} \quad , \quad (12)$$

$$\tilde{v}_x^{V,I} = \frac{v_x^{V,I}}{d_i^{V,I}} \quad , \quad \tilde{g}^{V,I} = \frac{g^{V,I}}{d_i^{V,I} C_{eq}^{V\times, I\times}} \quad . \quad (13)$$

Here S^{AC} and G^{AC} are the rates of impurity atom absorption due to the cluster formation and generation of separate impurity atoms during cluster dissolution, respectively; S^{AD} and G^{AD} are the rates of impurity atom absorption due to the formation of extended defects and generation of separate impurity atoms during extended defect annealing, respectively; $\tilde{C}^{V\times}$ and $\tilde{C}^{I\times}$ are the concentrations of vacancies and self-interstitials in the neutral charge state normalized to the equilibrium concentrations $C_{eq}^{V\times}$ and $C_{eq}^{I\times}$, respectively; $D^E(\chi)$ is the effective diffusivity of impurity atoms due to the vacancy—impurity pairs mechanism; $D^F(\chi)$ is the effective diffusivity of impurity atoms due to migration

of the pairs “impurity atom — self-interstitials” D_i^E and D_i^F are the intrinsic diffusivities; superscripts E and F denote the vacancy and interstitial pair diffusion mechanisms, respectively; $\beta_1^{E,F}$ and $\beta_2^{E,F}$ are the parameters describing respectively the relative contributions of singly and doubly charged point defects to the impurity transport; functions $a^{E,F}$ describe the overall influence of heavy doping on the local equilibrium between diffusing pairs, point defects and substitutionally dissolved dopant atoms and also between the point defects in different charge states; v_x^E and v_x^F are the projections onto the x -axis of the effective drift velocities of dopant atoms in the field of elastic stresses; χ is the concentration of charge carriers normalized to the intrinsic carrier concentration n_i ; C^B is the concentration of impurity with opposite type of conductivity; z^{Cl} and m are the cluster charge in units of the elementary charge and the number of doping atoms incorporated in the cluster; $d^{V,I}(\chi)$ and $d_i^{V,I}$ are respectively the effective and intrinsic diffusivities of point defects; superscripts V and I denote the vacancies and self-interstitials, respectively; $k^{V,I}$ and $\tau_i^{V,I}$ are the effective recombination coefficient and the average lifetime of the corresponding point defects, respectively; functions $a^{Vd,Id}$ describe the influence of heavy doping on the local equilibrium between point defects in different charge states; v_x^V and v_x^I are the projections onto the x -axis of the effective drift velocities of vacancies and self-interstitials in the field of elastic stresses, respectively; l_i^V and l_i^I are the average migration lengths of vacancies and self-interstitials, respectively; g_i^V and g_i^I are respectively the generation rates of vacancies and self-interstitials.

As follows from Ref. [4], to describe the impurity clustering during transient enhanced diffusion of As and P, one can use the expression

$$C^{AC} = K \tilde{C}_D \chi^{m-z^{Cl}} C^m \quad (14)$$

instead of Eq.(2), if the annealing duration is not very short (for example, annealing is longer than 1 s at a temperature of 1000 °C and higher). A similar expression can be used for the description of phosphorus clustering [12].

Here K is the constant of the cluster formation reaction; m is the number of impurity atoms incorporated in cluster; \tilde{C}_D is the relative concentration of nonequilibrium defects participating in clustering

$$\tilde{C}_D = \frac{(\tilde{C}_{D1})^{m_1}}{(\tilde{C}_{D2})^{m_2}} \quad , \quad \tilde{C}_{D1} = \frac{C^{D1\times}}{C_{eq}^{D1\times}} \quad , \quad \tilde{C}_{D2} = \frac{C^{D2\times}}{C_{eq}^{D2\times}} \quad , \quad (15)$$

where $C^{D1\times}$ and $C^{D2\times}$ are the concentrations of point defects D_1^\times and D_2^\times in the neutral charge states facilitating the cluster formation and generated during clustering, respectively; $C_{eq}^{D1\times}$ and $C_{eq}^{D2\times}$ are the equilibrium concentrations of these defects; m_1 and m_2 are respectively the numbers of point defects D_1 and D_2 participating in the cluster formation. Due to multiplier \tilde{C}_D in the expression (14), it is possible to take into account the influence exerted by the nonuniform distributions of nonequilibrium point defects on the clustering process and influence of the defect generation during clustering on transient enhanced diffusion. Thus, the expression (14) enables one to consider the coupled phenomenon of clustering and transient enhanced diffusion.

3 Analysis of equations

The set of Eqs.(1) — (6) can describe different processes of diffusion and chemical reactions in semiconductors including “uphill” impurity diffusion in the vicinity of the interface. The proposed equations take into account different charge states of all mobile and immobile species and also the drift of the mobile species in the built-in electric field and in the field of elastic stresses, although only the concentrations of neutral defects are given in the explicit form in these equations. The phenomenon of “uphill” diffusion can arise due to the direct absorption of impurity atoms by extended defects [6] or due to clustering in the near surface region, if these processes are nonequilibrium and proceed in the forward direction. To describe this phenomenon one can use Eqs.(2) and (3), respectively. Moreover, as can be seen from Eq.(4), the “uphill” impurity diffusion occurs due to the influence of stresses on the pair migration [10] or due to the formation of nonuniform distributions of point defects in the neutral charge state [13]. As it follows from Eqs.(5) and (6), the nonuniform distributions of vacancies and self-interstitials can be formed due to the absorption of point defects by the surface (interface) or by extended defects. Moreover, the nonuniform defects distributions can be formed due to the stress-mediated migration of vacancies and self-interstitials. Thus, a multifactor character of the “uphill” impurity diffusion in the near surface region follows from analysis of Eqs.(1) — (6), and it is difficult to determine which factor is dominant in the formation of the near surface peak of the impurity concentration. However, there is an experimental evidence that the silicon surface absorbs self-interstitials [5], which govern the transient enhanced diffusion. It means that in any case the formation of nonuniform distributions of point defects due to their absorption on the surface provides a certain contribution to the “uphill” impurity diffusion.

Using an analytical approach, let us evaluate the influence of the nonuniform neutral defect distribution on the “uphill” diffusion. Consider the case of TED governed by one species of nonequilibrium point defects, namely nonequilibrium self-interstitials. Let us suppose for simplicity that the concentration of an impurity providing the opposite type of conductivity is approximating zero $C^B \approx 0$ and $a^F \approx 1$. Also, suppose that during annealing the formation of neutral clusters or precipitates occurs. Then, in the region of high impurity concentration Eq.(4) takes the form

$$\frac{\partial C^T}{\partial t} = \frac{\partial}{\partial x} \left(2D^F(\chi) \tilde{C}^{I\times} \frac{\partial C}{\partial x} + D^F(\chi) C \frac{\partial \tilde{C}^{I\times}}{\partial x} \right) . \quad (16)$$

The first term in the right-hand side parentheses describes the impurity flux according to the Fick’s law, whereas the second one describes an additional flux arising due to the nonuniform defect distribution. If this flux is opposite to that due to the impurity concentration gradient, the phenomenon of “uphill” diffusion is observed.

For simplicity, we consider the case of long-time annealing. Then, a steady-state solution of Eq. (16) for $t \rightarrow \infty$ and $\frac{\partial C^T}{\partial t} \approx 0$ can be derived

$$2D^F(\chi) \tilde{C}^{I\times} \frac{\partial C}{\partial x} + D^F(\chi) C \frac{\partial \tilde{C}^{I\times}}{\partial x} = A = const . \quad (17)$$

Let us consider the structure “silicon-on-insulator” and suppose reflecting boundary

conditions for impurity atoms on the surface ($x = 0$) and at the interface ($x = x_R$). Then $A = 0$, and Eq. (17) can be written as

$$\frac{dC}{dx} = -b(x) C \quad , \quad (18)$$

where

$$b(x) = \frac{1}{2\tilde{C}^\times} \frac{d\tilde{C}^{I\times}}{dx} \quad . \quad (19)$$

We can solve Eq.(17) using the method of variable separation

$$\frac{dC}{C} = -b(x) dx \quad , \quad \int_{C_R}^C \frac{dC}{C} = - \int_{x_R}^x b(x) dx \quad , \quad (20)$$

$$C(x) = C_R \exp \left[\int_x^{x_R} b(x) dx \right] \quad , \quad (21)$$

where $C_R = C(x_R)$ is the impurity concentration at the interface.

Let us suppose for simplicity that the distribution of self-interstitials is approximately described by the solution of Eq.(6) with Dirichlet boundary conditions and constant equation coefficients taking the influence of stresses and generation of point defects in the near surface region as negligible

$$\tilde{C}^{I\times}(x) = \sinh^{-1} \left(\frac{x_R}{l_i^I} \right) \left[\tilde{C}_S^{I\times} \sinh \left(\frac{x_R - x}{l_i^I} \right) + \tilde{C}_R^{I\times} \sinh \left(\frac{x}{l_i^I} \right) \right] \quad , \quad (22)$$

where $\tilde{C}_S^{I\times}$ and $\tilde{C}_R^{I\times}$ are the normalized concentrations of point defects at the surface and interface, respectively.

Substituting expression (19) into (21), one can obtain

$$C(x) = C_R \exp \left[\frac{1}{2} \int_{\tilde{C}^{I\times}}^{\tilde{C}_R^{I\times}} \frac{d\tilde{C}^{I\times}}{\tilde{C}^{I\times}} \right] \quad . \quad (23)$$

Integral calculation in expression (23) gives

$$C(x) = C_R \exp \left[\frac{1}{2} \ln \left(\tilde{C}_R^{I\times} \right) - \frac{1}{2} \ln \left(\tilde{C}^{I\times}(x) \right) \right] = C_R \sqrt{\frac{\tilde{C}_R^{I\times}}{\tilde{C}^{I\times}(x)}} \quad . \quad (24)$$

It can be seen from expression (24) that the steady-state distribution of impurity atoms varies inversely as the square root from the normalized self-interstitial distribution $\tilde{C}^{I\times}(x)$. It means that for the defect distribution, similar to the distribution of (22) with $\tilde{C}_S^{I\times} \ll \tilde{C}_R^{I\times}$, i.e. in case of the absorption of self-interstitials at the surface, the “uphill” impurity diffusion and peak of impurity concentration adjacent to the surface must be observed. It follows from Eqs. (1) and (14) that this peak will be more pronounced in the case of significant clustering of impurity atoms.

4 Simulation results

Results of the previous analytical investigation are confirmed by the numerical simulation presented below. As an example, the redistribution of boron atoms implanted into silicon at low energy and high fluence is investigated. For comparison, the experimental data obtained by Lerch et al. [14] are used. In Ref. [14] boron ions were implanted into n-type silicon substrates of the resistivity 10-20 Ωm and orientation (100) at the energy of 1 keV and fluence $Q = 1.0 \times 10^{15} \text{ cm}^{-2}$. The annealing process was carried out at a temperature of 1050 $^{\circ}\text{C}$ with duration of 10 s. The concentration profile of the boron atom distribution was measured by SIMS. This concentration profile is presented in Fig. 1 together with the profile calculated by means of the set of equations obtained.

The finite-difference method [15] is used to find a numerical solution of this system of equations. The present paper chooses a more stable implicit method to avoid numerical instability. Following [15], the right-hand side of Eq.(4) and two first terms on the left-hand side of Eq.(6) which describe the diffusion of dopant atoms and self-interstitials, respectively, are approximated by a symmetric difference operator of second order accuracy on the space variable x . To solve the system of the obtained nonlinear algebraic equations we use the simplest iterative technique substituting the values of the dopant concentration and concentration of neutral self-interstitials determined on the previous iteration into the coefficients of nonlinear algebraic equations.

During simulation it was supposed that transient enhanced diffusion of the boron implanted into silicon substrate occurred due to the kick-out diffusion mechanism that is mathematically equivalent to the pair diffusion mechanism [16]. We have used the following parameters to describe ion implantation and diffusion of the dopant atoms and point defects: $Q = 1.0 \times 10^{15} \text{ cm}^{-2}$; $R_p = 0.00512 \mu$; $\Delta R_p = 0.0038 \mu$; $Sk = 0.3$; $n_i = 1.166 \times 10^7 \mu^{-3}$; $D_i \tilde{C}_{\text{max}}^{I \times} = 1.3 \times 10^{-05} \mu^2/\text{s}$; $\beta_1^I = 0.7$; $\beta_2^I = 0$; $\tilde{C}_{S \text{max}}^{I \times} = C_S^{I \times} / C_{\text{max}}^{I \times} = 0.04$ a.u.; $l_i^I = 0.02 \mu$. Here R_p is the average projected range of dopant ions; ΔR_p is the straggling of the projected range; Sk is the skewness of boron distribution as implanted; D_i is the intrinsic diffusion coefficient of boron; $\tilde{C}_{\text{max}}^{I \times} = C_{\text{max}}^{I \times} / C_{eq}^{I \times}$ is a maximum value of the normalized self-interstitial concentration; $C_{\text{max}}^{I \times}$ is a maximum value of the neutral self-interstitial concentration in the region of impurity diffusion; $C_S^{I \times}$ is the concentration of neutral self-interstitials at the surface. The value of equilibrium boron diffusivity at 1050 $^{\circ}\text{C}$ known from literature $D_i = 4.098 \times 10^{-6} \mu^2/\text{s}$ [17]. This means that the time average enhancement of boron diffusion due to the nonequilibrium self-interstitials is approximately 3.2 fold.

As can be seen from Fig. 1, the measured boron profile is characterized by the formation of a local peak of the impurity concentration near the surface due to the distinct “uphill” diffusion. It is interesting to note that the impurity profiles calculated by means of the computer code SSUPREM-IV included in the desktop program (framework) Athena which are presented in [14] do not describe this phenomenon. In our opinion, this discrepancy with the experiment in the near surface region is due to neglecting the interface effect on the defect subsystem that is absolutely inappropriate for the models intended to simulate shallow doped layers. It was shown in [5] that the semiconductor surface absorbs nonequilibrium self-interstitials governing the transient enhanced diffusion of the ion-implanted impurity. As can be seen from expression (24) and numerical calculations presented in Fig. 1, taking into account the phenomenon of self-interstitial absorption

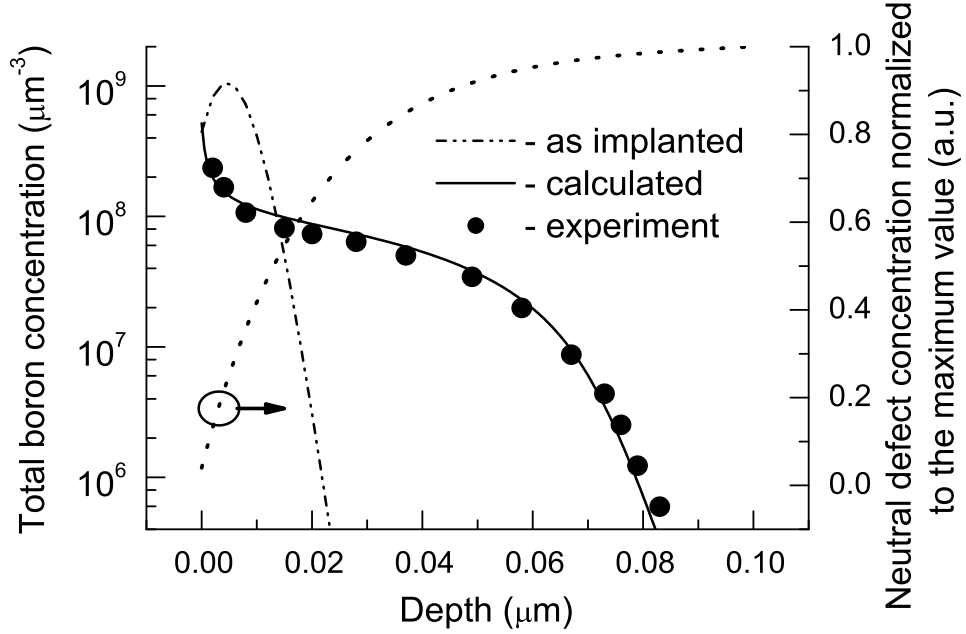


Figure 1: Calculated concentration profile of ion-implanted boron after thermal annealing during 10 s at a temperature of 1050 °C. Solid line — calculated distribution of the total boron concentration after annealing; dash-dotted line — distribution of boron after ion implantation; dotted line — time average distribution of self-interstitial concentration. Circles represent the experimental data taken from Lerch et al. [14].

enables one to explain the formation of a near surface peak of the impurity concentration and provides a good agreement of the calculated impurity profile with the experimental data. It is interesting to note that absorption of boron atoms by extended defects in the near surface region also can contribute to the “uphill” diffusion. In this case the nonuniform self-interstitial distribution with decreased concentration gradient can be used to explain the experimental data.

5 Conclusion

For adequate simulation of the transient enhanced diffusion near the surface or at the interface of ion-implanted layers the set of equations describing impurity diffusion and quasichemical reactions of the dopant atoms and defects was proposed and analyzed. The proposed diffusion equations take into account different charge states of mobile and immobile species and drift of the mobile species in the built-in electric field and the field of elastic stresses, although in these equations only the concentrations of neutral defects are given in the explicit form. The absorption of self-interstitials on the surface and drift of mobile defects due to elastic stresses result in the nonuniform distributions of point defects. It was shown, analytically and by means of numerical calculations, that consideration of the nonuniform defect distributions makes it possible to explain the phenomenon of “uphill” impurity diffusion near the surface during annealing of the ion-implanted layers. The performed calculations of the boron concentration profile after annealing of a shallow implanted layer agree well with the experimental data including the near surface region, where the formation of a concentration peak occurs. The agreement with experiment confirms the efficiency of the proposed equations for simulation of shallow layer annealing.

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